Revolutionising Environmental Monitoring Technologies: Key Barriers and Possible Solutions

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S4: Nanotechnology’s role for a sustainable environment (water, soil, air)
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Dublin & DCU Location
Insight Centre for Data Analytics

- Biggest single research investment ever by Science Foundation
- Biggest coordinated research programme in the history of the state
- Focus is on ‘big data’
Funded under grant agreement No. 604241 of the European Union’s Seventh Framework Programme
‘Grand Challenge for Analytical Chemistry’

• “A ‘Grand Challenge’ posed for analytical chemistry is to develop a capability for sampling and monitoring air, water and soil much more extensively and frequently than is now possible”

• “Such goals will require improvements in sampling methodology and in techniques for remote measurements, as well as approaches that greatly lower per-sample and per-measurement costs”

Royce Murray, Editorial, Analytical Chemistry, February 2010
Remote (Continuous) Sensing Challenges: Platform and Deployment Hierarchies

**Physical Transducers** – low cost, reliable, low power demand, long life-time

Thermistors (temperature), movement, location, power, light level, conductivity, flow, sound/audio, ....

**Chemical Sensors** – more complicated, need regular calibration, more costly to implement

Electrochemical, Optical, .. For metal ions, pH, organics...

**Biosensors** – the most challenging, very difficult to work with, die quickly, single shot (disposable) mode dominant use model

Due to the delicate nature of biomaterials enzymes, antibodies....

**Increasing difficulty & cost**

**Increasing scalability**

**Gas/Air Sensing** – easiest to realise

Reliable sensors available, relatively low cost

Integrate into platforms, develop IT infrastructure, GIS tools, Cloud Computing

**On-land Water/ Monitoring**

More accessible locations

Target concentrations tend to be higher

Infrastructure available

**Marine Water**

Challenging conditions

Remote locations & Limited infrastructure

Concentrations tend to be lower and tighter in range
Argo Project (accessed March 9 2014)

- Ca. 3,600 floats: temperature and salinity
- Only 216 reporting chem/bio parameters (ca. 6%)
- Of these nitrate (38), DO (202), Bio-optics (43), pH (3)
  DO is by Clark Cell (Sea Bird Electronics) or Dynamic fluorescence quenching (Aanderaa)

See https://picasaweb.google.com/JCOMMOPS/ArgoMaps?authuser=0&feat=embedwebsite

‘calibration of the DO measurements by the SBE sensor remains an important issue for the future’, Argo report ‘Processing Argo OXYGEN data at the DAC level’, September 6, 2009, V. Thierry, D. Gilbert, T. Kobayashi
Control of membrane interfacial exchange & binding processes

Remote, autonomous chemical sensing is a tricky business!
Direct Sensing vs. Reagent Based LOAC/ufluidics

Direct Sensing

outside world

sensor

signal

clearing

sample

molecular interactions

LOAC Analyser

reagents

sample, standards

source

Reaction manifold

detector

waste

s

sample

BL

blank

BL
2\textsuperscript{nd} Generation Analyser: Design

Sampling port
Deployment at Osberstown WWTP

- Phosphate monitoring unit deployed
- System is fully immersed in the treatment tank
- Wireless communications unit linked by cable
- Data transmitted to web

Slide 11
Autonomous Chemical Analyser

49-Day Trial at Waste Water Treatment Plant

Phosphate monitoring using the Yellow Method
Osberstown – 3 week deployment

Biofouling of sensor surfaces is a major challenge for remote chemical sensing – both for the environment and for implantable sensors
Cost Comparison Analyser (€)

- Gen1
- Gen2
- Future

- Fluidics
- Electronics
- Housing
Multi-Functional Fluidics

• At present, the fluidic system’s function is to;
  – Transport reagents, samples, standards to the detector
  – Perform relatively simple (but important) tasks like cleaning, mixing
  – Switching between samples, standards, cleaning solutions

• In the future, the fluidic system will perform much more sophisticated ‘bio-inspired’ functions
  – System diagnostics, leak/damage detection
  – Self-repair capability
  – Switchable behaviour (e.g. surface roughness, binding/release),

• These functions will be inherent to the channels and integrated with circulating smart micro/nano-vehicles
  – Spontaneously move under an external stimulus (e.g. chemical, thermal gradient) to preferred locations
  – Perform complex tasks on arrival
Extend Period of Use via Arrays of Sensors….?

- If each sensor has an in-use lifetime of 1 week....
- And these sensors are very reproducible....
- And they are very stable in storage (up to several years)....

Then 50 sensors when used sequentially could provide an aggregated in-use lifetime of around 1 year.

But now we need multiple valves integrated into a fluidic platform to select each sensor in turn.
How to advance fluid handling in LOC platforms: re-invent valves (and pumps)!

- Conventional valves cannot be easily scaled down - Located off chip: fluidic interconnects required
  - Complex fabrication
  - Increased dead volume
  - Mixing effects
- Based on solenoid action
  - Large power demand
  - Expensive

Solution: soft-polymer (biomimetic) valves fully integrated into the fluidic system
Famous Molecule....

From Prof. Thorfinnur Gunnlaugsson, TCD School of Chemistry
Spotted on Nickelodeon Cartoons February 2015
Poly($N$-isopropylacrylamide)

- pNIPAAm exhibits inverse solubility upon heating
- This is referred to as the LCST (Lower Critical Solution Temperature)
- Typically this temperature lies between 30-35°C, but the exact temperature is a function of the (macro)molecular microstructure
- Upon reaching the LCST the polymer undergoes a dramatic volume change, as the hydrated polymer chains collapse to a globular structure, expelling the bound water in the process

![pNIPAAm structure](image)

Hydrophilic

Hydrated Polymer Chains

$\Delta T$

Hydrophobic

Loss of bound water -> polymer collapse
Polymer based photoactuators based on pNIPAAm

Figure 3. (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was (○, red) 0, (☑) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in (○) non-irradiated and (☑) irradiated region as a function of time after 3 s blue light irradiation.

poly(N-isopropylacrylamide) (PNIPAAm)
Formulation as by Sumaru et al
Reversible Photo-Switching of Flow

Above: scheme showing switching process protonated MC-H+ photoswitched to SP triggering p(NIPAM-co-AA-co-SP) gel contraction and opening of the channel.

Right, Top: Photos of the valve in operation before (flow OFF) and after (flow ON) one minute of blue light irradiation.

Right, Bottom: Flowrate and cumulative volume measurements showing repeated opening and closing of microvalve: 1 min blue light irradiation opens valve followed by ~5.5 min thermal relaxation to close.

From: ‘Molecular design of light-responsive hydrogels, for in-situ generation of fast and reversible valves for microfluidic applications’ (submitted for publication)

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Photocontrol of Assembly and Subsequent Switching of Surface Features

Photoswitchable Ratchet Surface Topographies Based on Self-Protonating Spiropyran—NIPAAm Hydrogels

Jelle E. Stumpel, Bartosz Ziółkowski, Larisa Florea, Dermot Diamond, Dirk J. Broer, and Albertus P. H. J. Schenning

High crosslink density

Low crosslink density

Light source

\( \lambda = 455 \text{ nm} \)

acrylic acid, 5 mol%  MBIS, 1-2 mol%  Darocur 1173, 1 mol%

\( \lambda = 455 \text{ nm} \)
Time to re-think the game!!

• New materials with exciting characteristics and unsurpassed potential...

• Combine with emerging technologies and techniques for exquisite control of 3D morphology

• And greatly improved methods for characterisation of structure and activity

We have the tools – now we need creativity!
The European Sensor Systems Cluster (ESSC)

European Sensor Systems Cluster - ESSC
Vision, Objectives, Strategies, Priorities and Challenges of EU Cluster
Cluster launched at Preparatory Workshop on 27 November 2014 in Brussels
sponsored and observed by EC DG Research and Innovation

AMA Conference 2015 - SENSOR+TEST Trade Fair
Room Tunis, Session Time: 12:00 - 13:30

Nuremberg/Germany, 19 May 2015

Vision, Objectives and Position Paper

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